

Probing soft nanostructured interfaces with x-rays

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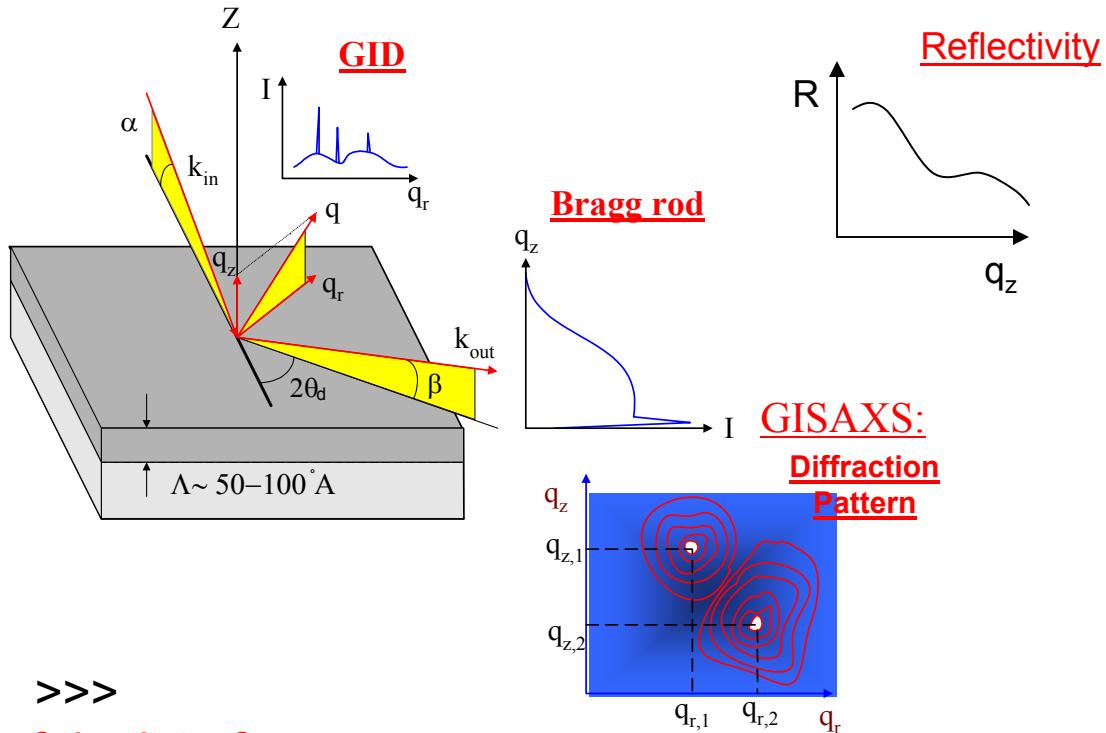


Diblock polymer films: order formation.

Liquid on nano-patterned surfaces: microscopic picture.

Nanoparticles in nano-thick liquids.

Experimental Tools



X-ray reflectivity >>>

e-Density profile of the interface

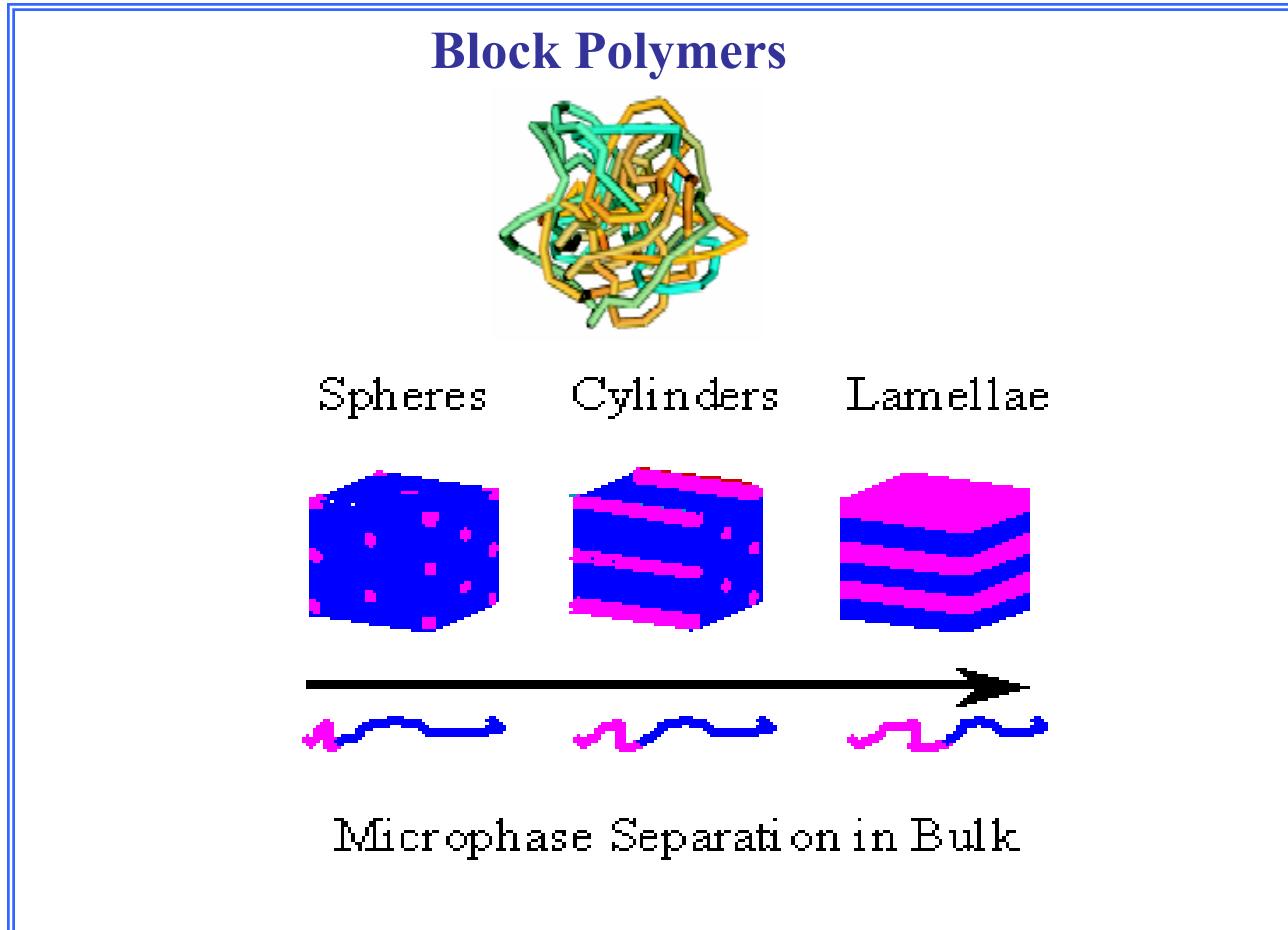
X-ray Grazing Incidence Diffraction (GID) >>>

In-plane structure of 2D ordered system

Grazing Incident Small Angle X-ray Scattering (GISAXS) >>>

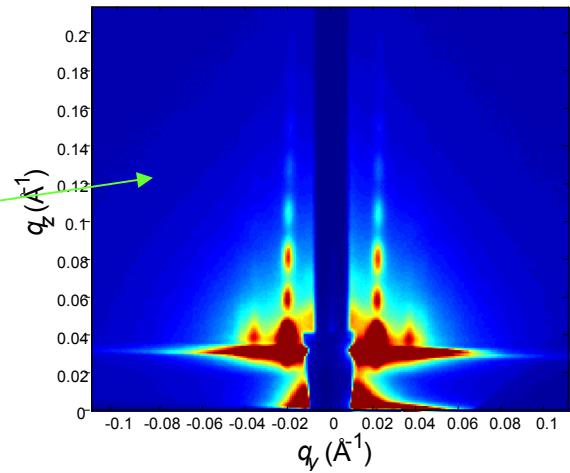
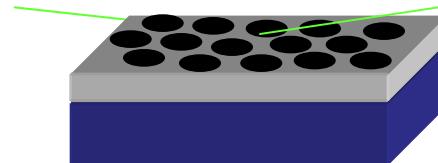
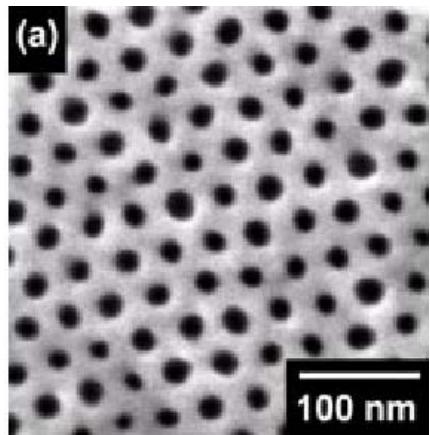
Structure of thin films (1-1000's nm)

Self-assembled diblock copolymers at surfaces

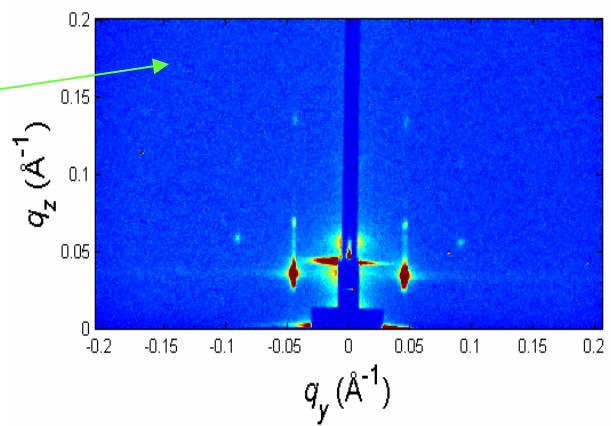
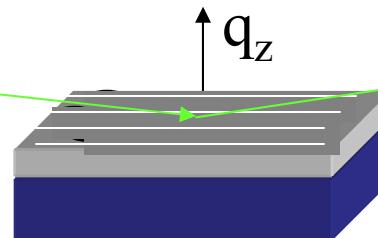
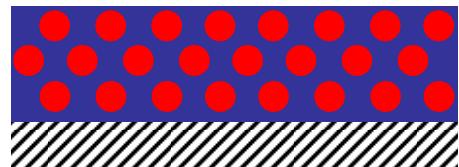


Hexagonal Phase Orientation

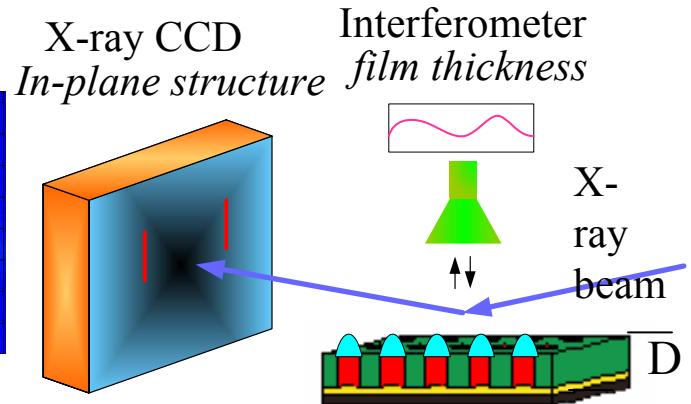
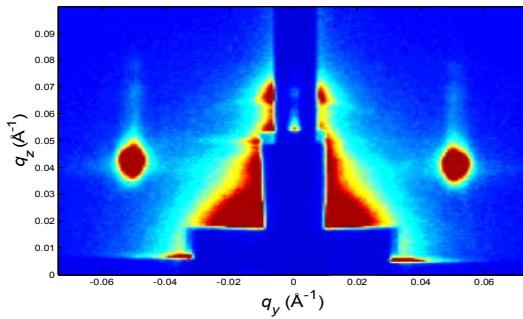
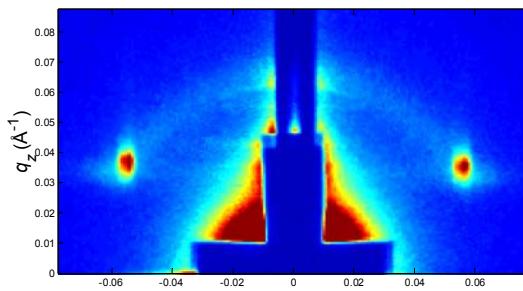
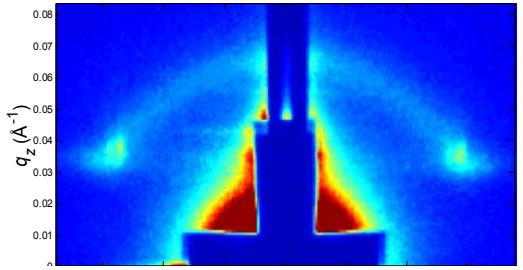
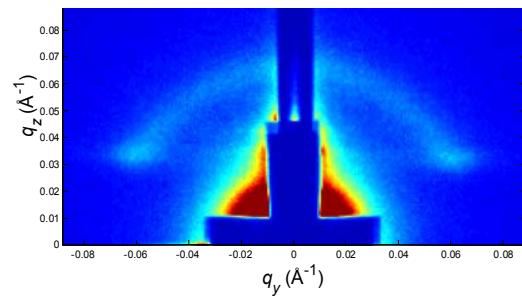
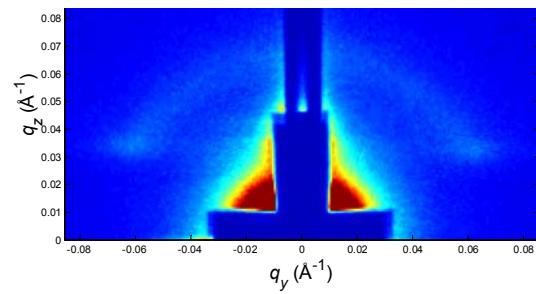
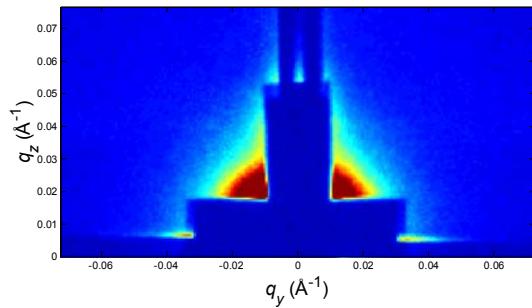
Standing-up phase



Lying down phase



Ordering formation from the solution



- Surface X-ray scattering and optical interferometry allow in-situ studying of film formation
- Liquid-like ordering is detected at $\sim 15\%$ of solvent
- Crystal-like ordering is observed $\sim 3\text{-}5\%$ of solvent

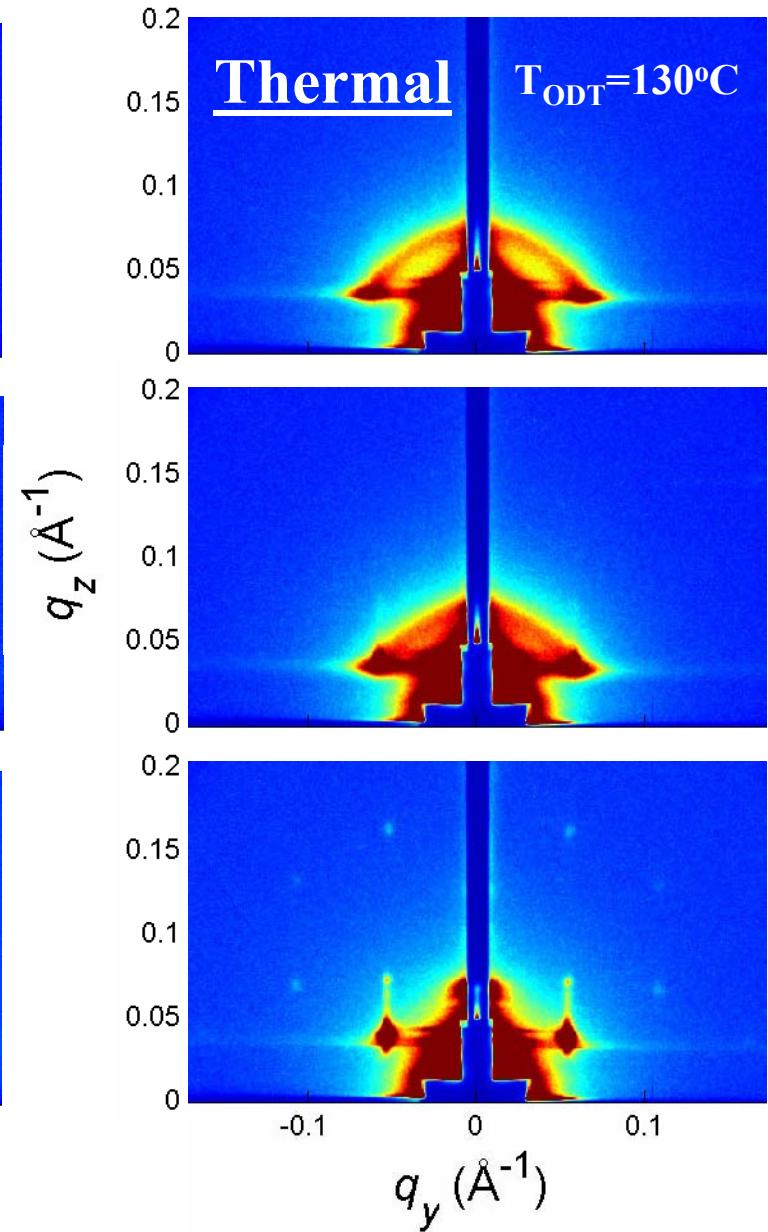
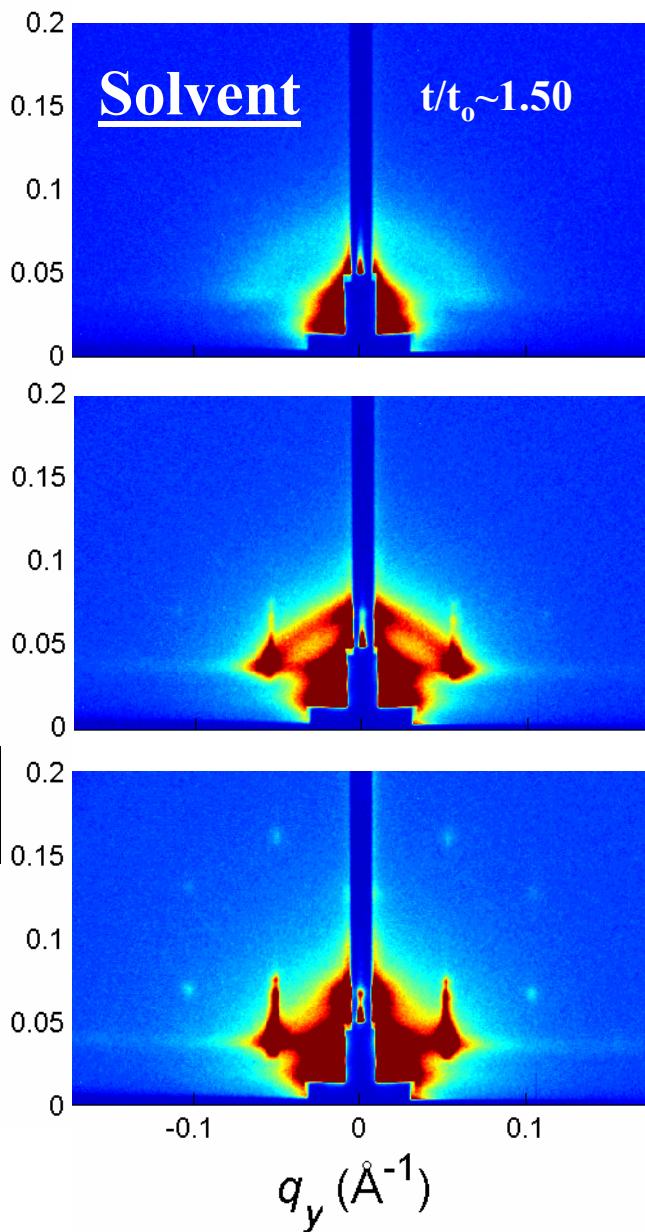
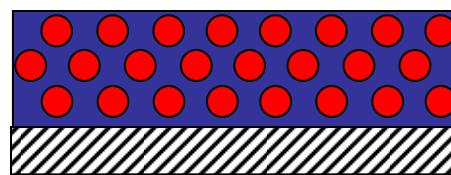
Order/disorder Transitions: solvent or thermal

PEP-*b*-PLA

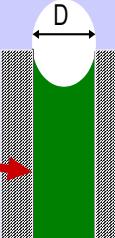
Thickness
measured with
interferometer

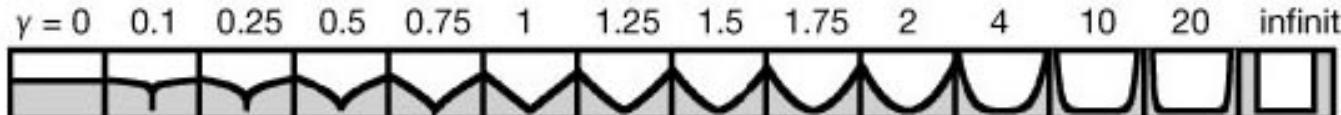
Order sets in
below a critical
conc.

$q_z (\text{\AA}^{-1})$



Liquids on geometrical nano-patterned surfaces: microscopic view

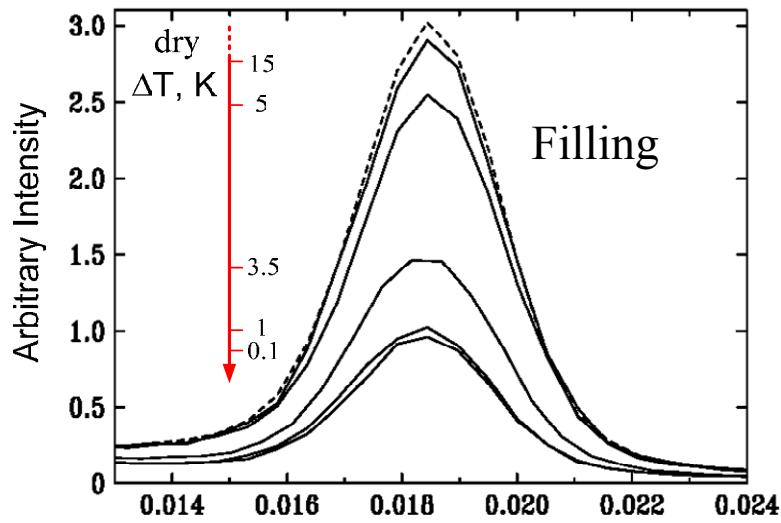
Flat surfaces - Complete Wetting	Structured surface- ?	Slits, porous media - Capillary condensation
 $l \sim \Delta\mu^{-\beta}$ <p>$\beta = 1/3$, for dispersion forces</p> <p>Depends on microscopic interactions</p>	 <p><i>Depends on both.</i> <i>Depends on the shape</i></p>	 $\Delta\mu^* = \frac{-2\gamma}{(\rho_l - \rho_g)D}$ <p>Geometry dominated</p>



- M. O. Robbins et al, Phys. Rev. A **43**, 4344 (1991)
 C. Rascon and A. O. Parry, Nature **407**, 986 (2000)
 C. Bauer C, S. Dietrich, Phys. Rev E, 1664 (2000)

Filling of surface cavities

In-plane diffraction

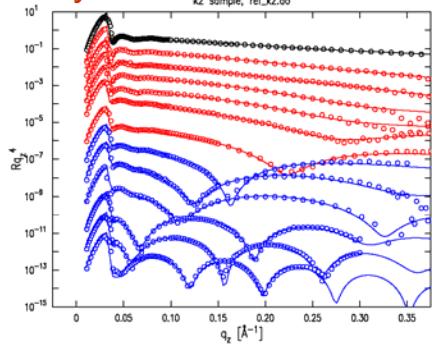


X-ray reflectivity from

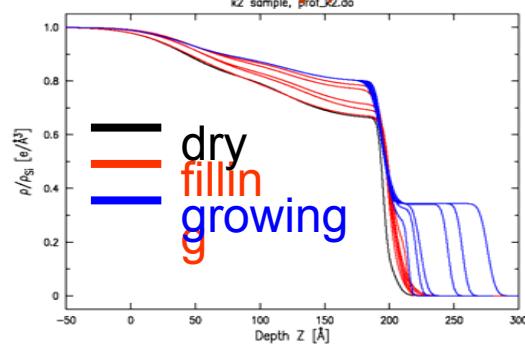
$q_{xy} (\text{\AA}^{-1})$

Normal to surface

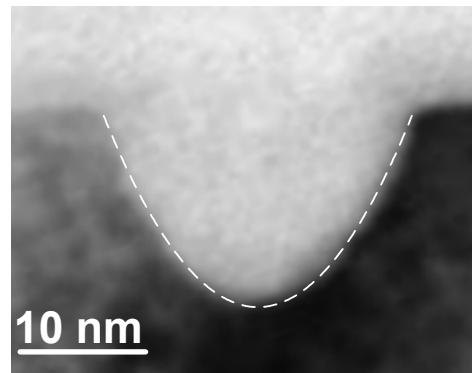
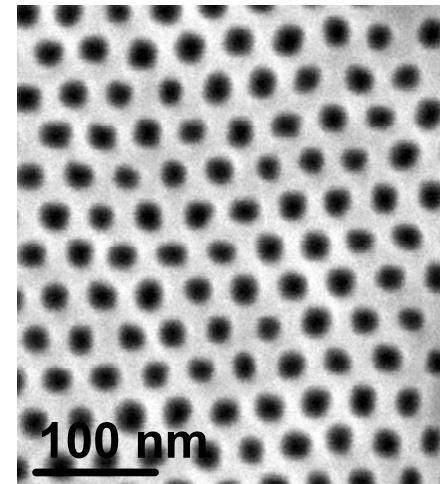
dry and wet surfaces



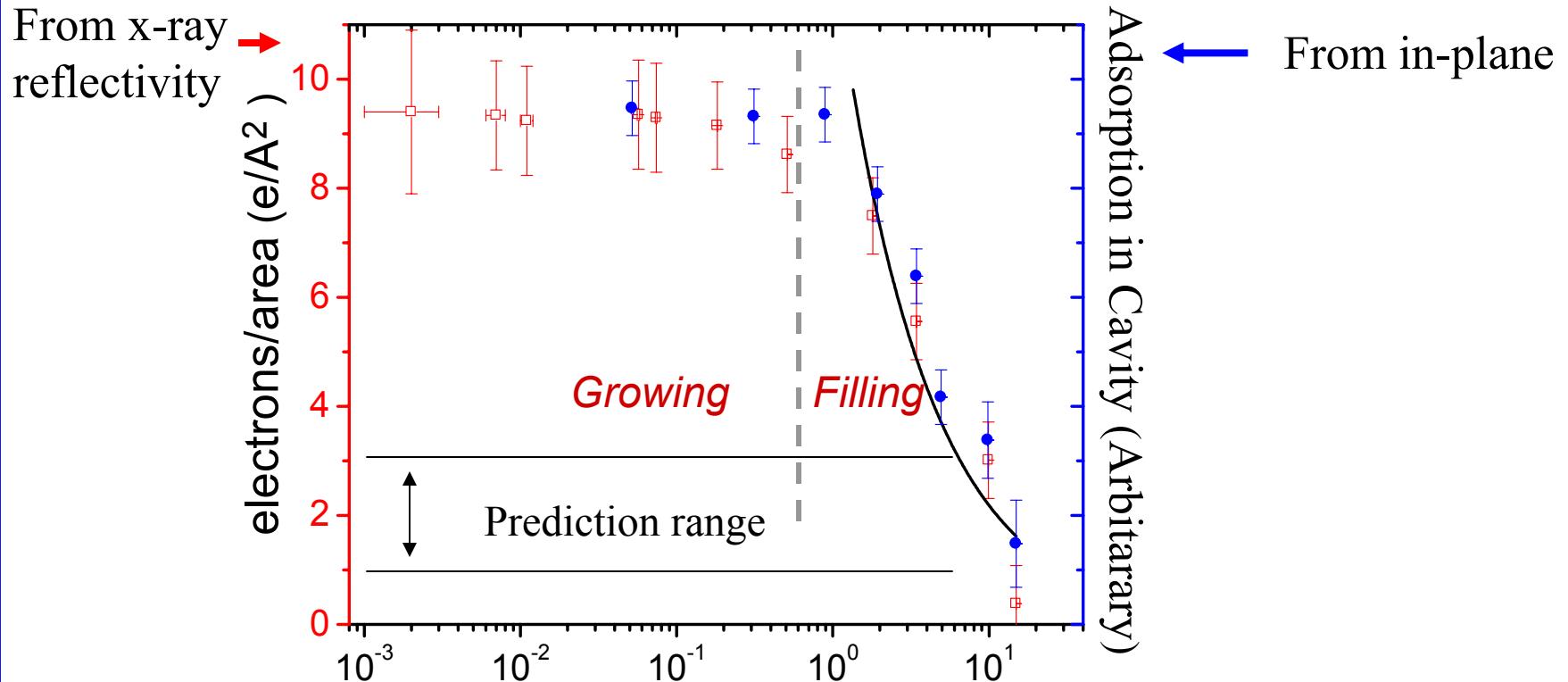
Electron-density profile



- How nano-cavities are filled with liquid?

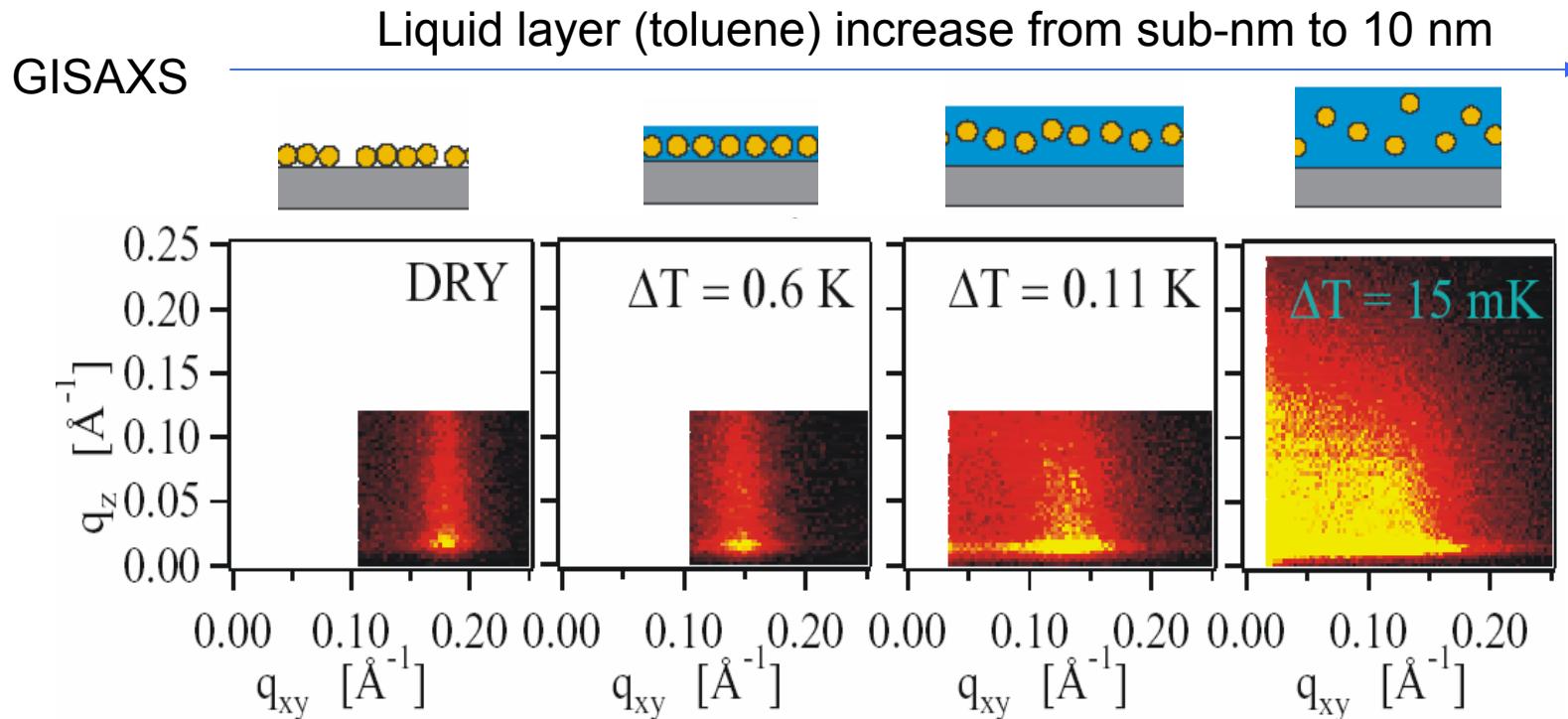


Filling of nano-cavities



- **Filling** with liquids, while the top liquid layer remains thin (<1 nm)
- Similar filling exponent $\beta = -0.76$ obtained from reflectivity and in-plain
- β differs from the theoretical prediction, suggesting finite-size effects

Nanoparticles assemblies in thin liquid films



- *Thin (<2nm)* adsorbed liquid films improve the nanoparticle (Au-thiols, 4 nm) monolayer uniformity and increase the in-plane order.
- *Thicker* films of good solvent initiate the dissolution of the monolayer—the transition from a 2D system to a 3D colloidal fluid is observed.

Summary

- Combination of surface scattering techniques probes scales from molecular size to 100's nm.
- Study of surface nano-systems (diblock polymers, nanoparticles, liquid films) under environmental conditions.
- For kinetics of self-assembly there is a need:
 - Faster 2D detectors
 - Quantitative analysis: software for managing large data sets, batch analyzing of images, modeling